



## Optimization of Pyrolysis for MgO Recycling in Magnesia-Based Flue Gas Desulfurization

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The magnesia (MgO)-based flue gas desulfurization process can effectively remove sulfur dioxide and the absorbent-MgO can be recycled *via* the pyrolysis of the major flue gas desulfurization byproduct MgSO<sub>3</sub>. In the current study, the pyrolysis conditions of the flue gas desulfurization byproducts was optimized to achieve efficient MgO recycling in the laboratory. The optimal pyrolysis conditions were 550 °C and 10 K/min heating rate. The dried MgSO<sub>3</sub> was found to have higher decomposition efficiency than the sample with moisture. The decomposition efficiency of MgSO<sub>3</sub> reached 90 %, whereas the MgO content in the pyrolyzed product reached 70 % and had ideal reactivity. The actual byproducts from the power plant were also pyrolyzed under the optimal conditions and compared with the MgSO<sub>3</sub> samples produced in laboratory. Given the existence of impurities, the pyrolysis effect of the actual byproducts was slightly inferior to the laboratory-produced MgSO<sub>3</sub>. Therefore, the impurity content of the byproducts must be decreased to efficiently recycle MgO.

**Key Words:** Magnesia-based flue gas desulfurization, Pyrolysis, MgO, Reactivity.

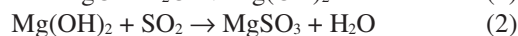
### INTRODUCTION

The combustion of fossil fuels such as coal and oil releases sulfur dioxide to the atmosphere. Sulfur dioxide is an important compound that contributes to acid wetting. Power plants driven by fossil fuels produce huge amounts of flue gas that are high in SO<sub>2</sub> content. Tall flue gas stacks disperse emissions by diluting pollutants in ambient air and transporting them to other regions<sup>1-3</sup>. Given that stringent environmental regulations on SO<sub>2</sub> emissions have been enacted in many countries, SO<sub>2</sub> is now being removed from flue gases by a variety of methods<sup>4-6</sup>. Various flue gas desulfurization technologies control SO<sub>2</sub> emissions from power plants<sup>7</sup>. Wet scrubbing is effective in removing SO<sub>2</sub> from flue gas using an alkaline sorbent slurry, usually limestone, lime, or magnesia (MgO), to scrub SO<sub>2</sub> containing flue gas<sup>8</sup>. In the wet-scrubbing flue gas desulfurization process, hot flue gas is made to contact a fine spray of lime slurry in a chamber and the sprayed slurry simultaneously absorbs SO<sub>2</sub><sup>9,10</sup>. SO<sub>2</sub> scrubbing technologies produce enormous quantities of byproducts, such as gypsum and MgSO<sub>3</sub><sup>11</sup>. Though these flue gas desulfurization byproducts can be used as fertilizers in farming, they also cause secondary pollution in high amounts, considering the increasing demand for SO<sub>2</sub> removal<sup>12-15</sup>.

An alternative to SO<sub>2</sub> removal is the MgO-based flue gas desulfurization process, wherein MgO is used as the desulfurizer. The amount of solid waste MgSO<sub>3</sub> is significantly reduced *via* the recycling of MgO, consequently protecting

the environment. By recycling MgO, sulfur can be recovered in the form of commercial-quality sulfuric acid<sup>16</sup>. Hence, the optimization of the conditions of desulfurizer regeneration is very important in increasing the efficiency of the MgO-based flue gas desulfurization process. The SO<sub>2</sub>-absorber MgO can be effectively recycled *via* the pyrolysis of the flue gas desulfurization primary byproduct MgSO<sub>3</sub><sup>17</sup>. Indeed, MgO-based flue gas desulfurization produces almost no solid waste and is a promising desulfurization process causing no secondary pollution.

In the MgO-based flue gas desulfurization process for absorbing SO<sub>2</sub> in flue gas, MgO first reacts with H<sub>2</sub>O. An Mg(OH)<sub>2</sub> slurry is then produced to neutralize the H<sub>2</sub>SO<sub>3</sub> from the reaction of SO<sub>2</sub> and H<sub>2</sub>O. Besides the primary byproduct MgSO<sub>3</sub>, MgSO<sub>4</sub> is also produced, which should be inhibited to achieve an efficient MgO recycling. After crystallization, dehydrolysis, as well as drying, MgSO<sub>3</sub> is pyrolyzed and then converted into MgO. This conversion process releases high concentrations of SO<sub>2</sub> that can be used as a raw material in manufacturing sulfuric acid. The highly reactive regenerated MgO can be recycled in the flue gas desulfurization process. The reactions in the MgO-based flue gas desulfurization process are as follow:



Given the existence of SO<sub>3</sub> in flue gas, a low amount of MgSO<sub>4</sub> is also produced:



As mentioned earlier, the desulfurizer MgO can be regenerated *via* the pyrolysis of the flue gas desulfurization byproduct MgSO<sub>3</sub>. The yield and reactivity of the regenerated MgO are significantly influenced by the pyrolysis temperature. Overheating sinters the MgO particles and blocks the pores of MgO, consequently decreasing its reactivity<sup>16</sup>. In the present study, the pyrolysis process of MgSO<sub>3</sub> is optimized to efficiently recycle MgO.

## EXPERIMENTAL

To investigate the effects of pyrolysis conditions on MgO regeneration, high purity MgSO<sub>3</sub> was used. An MgSO<sub>3</sub> sample was produced from the reaction of MgCl<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub>. The prepared sample contained 70-80 % MgSO<sub>3</sub> and 6-10 % MgSO<sub>4</sub>. Fig. 1 illustrates the experimental apparatus.

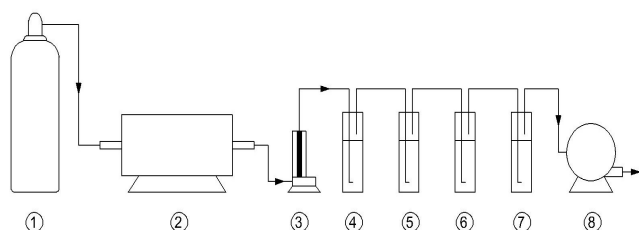


Fig. 1. Schematic diagram of the experimental apparatus. (1) Nitrogen cylinder. (2) Tubular oven with quartz tube. (3) Rotor flowmeter. (4) and (5) Flask with SO<sub>2</sub> absorber. (6) and (7) Flask with NaOH. (8) Vacuum pump

The effects of the pyrolysis temperature and moisture content on MgSO<sub>3</sub> pyrolysis were investigated. The MgSO<sub>3</sub> sample was pyrolyzed in the tubular oven. The pyrolysis temperature was automatically controlled. The SO<sub>2</sub> generated by the pyrolysis was absorbed by the liquid in the flask. The system was aerated by nitrogen. The reactivity of the regenerated MgO was characterized by X-ray diffraction as well as the hydration and citric acid methods to investigate the effect of pyrolysis conditions on MgO reactivity. Subsequently, the actual byproducts (50 % MgSO<sub>3</sub> and 20 % MgSO<sub>4</sub>) of the flue gas desulfurization from the power plant were pyrolyzed under the optimal conditions.

The SO<sub>2</sub> and MgO yields from the pyrolysis were calculated as follow:

$$\text{SO}_2 \text{ yield} = (m_1 - m_2) / \left( \frac{64}{104} a \cdot m_1 \right) \quad (5)$$

$$\text{MgSO}_3 \text{ decomposition percentage} = m_2 b / \left( \frac{40}{104} a \cdot m_1 \right) \quad (6)$$

where,  $m_1$  and  $m_2$  are the masses of the flue gas desulfurization by-products before and after pyrolysis,  $a$  is the MgSO<sub>3</sub> content of the flue gas desulfurization byproducts and  $b$  is the MgO content in the pyrolysis product.

### Activity test of MgO

**Hydration method:** In a weighting bottle ( $\phi$  40 mm  $\times$  40 mm),  $2 \pm 0.001$  g of specimen was added and mixed with

20 mL of distilled water, then covered with a small gap. At  $20 \pm 2$  °C and relative humidity of  $70 \pm 5$  %, the samples were allowed to settle for 15 min for hydration and the activity of MgO was measured by the pH changes of the solution with time. Two specimens were simultaneously run.

**Citric acid method:** About  $1.7 \pm 0.001$  g of specimen was placed in a dry beaker, which was then placed on a magnetic stirrer platform (500 r/min). A 200 mL standard solution of citric acid with two drops of phenolphthalein as indicator was quickly added to the beaker at 40 °C. The time of colour change was recorded using a stopwatch. When the test solution turned to red, the watch was stopped. The activity of MgO was measured by this timed event. Two specimens were simultaneously run.

## RESULTS AND DISCUSSION

### Effect of the pyrolysis temperature on the SO<sub>2</sub> yield:

Fig. 2 shows the effect of the pyrolysis temperature on the SO<sub>2</sub> yield. The SO<sub>2</sub> yield from the flue gas desulfurization decomposition of MgSO<sub>3</sub> increased with increased temperature. The SO<sub>2</sub> yield significantly increased and reached 92 % when the temperature reached 550 °C. When the temperature was increased from 600 to 1000 °C, the SO<sub>2</sub> yield did not change and was between 93-99.5 %. This result indicated that most of the MgSO<sub>3</sub> decomposed below 550 °C. The thermogravimetry (TG) curves in Fig. 3 shows the same results. The flue gas desulfurization byproducts started to decompose at about 200 °C, first losing crystallized water. The TG curve dramatically dropped when the temperature reached 400 °C, indicating that MgSO<sub>3</sub> started to decompose at 400 °C. The TG curve became flat when the temperature reached 550 °, indicating the near completion of MgSO<sub>3</sub> decomposition.

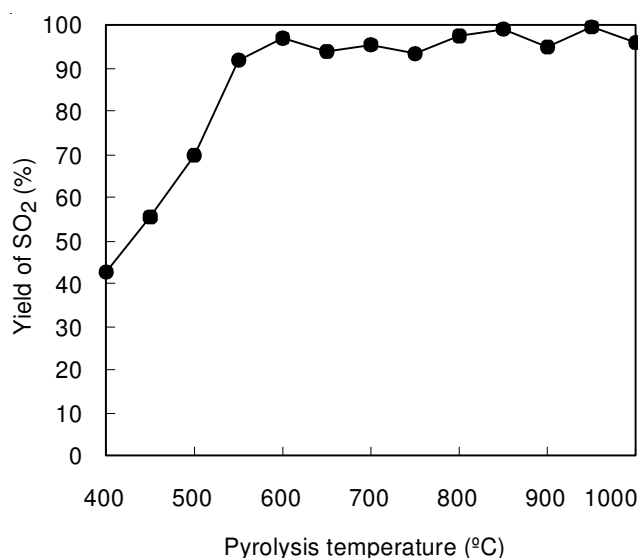


Fig. 2. Effect of the pyrolysis temperature on the SO<sub>2</sub> yield

**Effect of the pyrolysis temperature on MgSO<sub>3</sub> decomposition:** Figs. 4 and 5 show the effects of pyrolysis temperature on MgO yield and MgSO<sub>3</sub> decomposition. Both curves have similar trends, wherein the yield and decomposition percentage gradually increased with increased temperature. MgSO<sub>3</sub>

decomposition percentage was almost constant until 550 °C, suggesting the completion of the pyrolytic process.

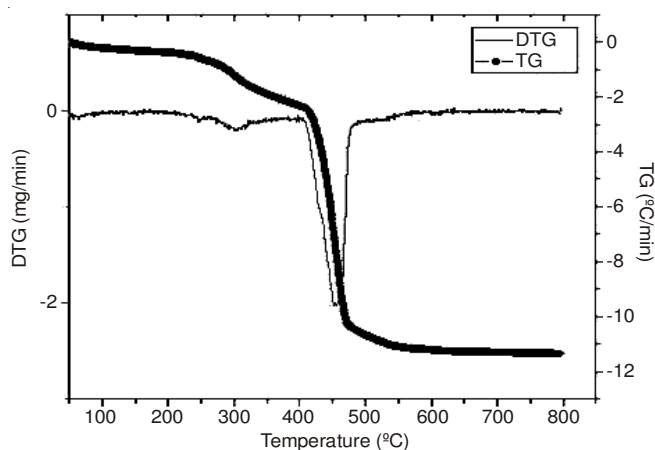


Fig. 3. Thermogravimetry curves of MgO-based flue gas desulfurization by-product decomposition

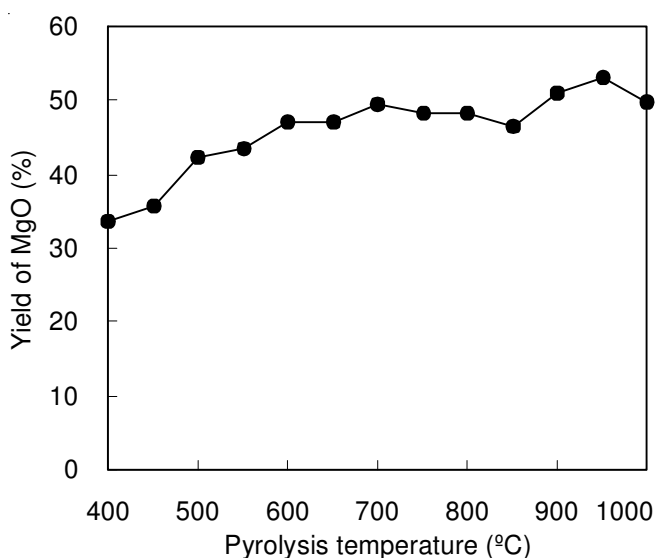


Fig. 4. Effect of pyrolysis temperature on the MgO yield

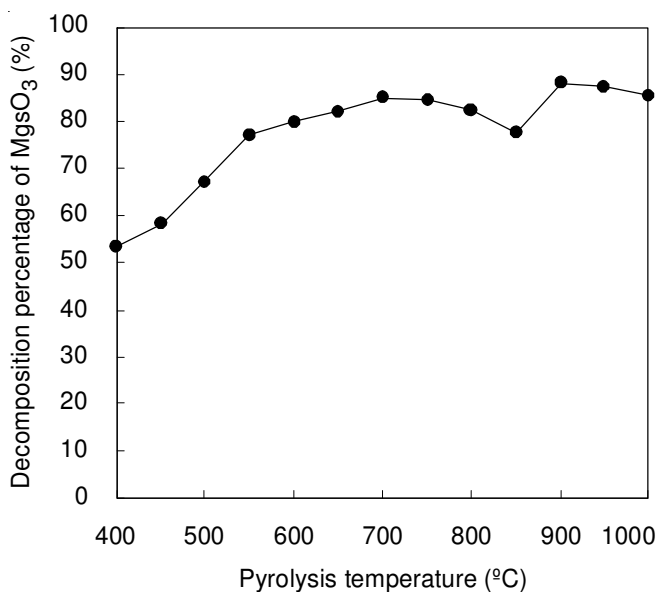


Fig. 5. Effect of pyrolysis temperature on MgSO<sub>3</sub> decomposition

**Effect of pyrolysis temperature on MgO reactivity:** The simplified hydration and citric acid methods were used to evaluate the reactivity of the regenerated MgO. The increased MgO hydration solution pH suggested the generation of Mg<sup>2+</sup> and OH<sup>-</sup>, which characterized the reactivity of MgO. Fig. 6 shows that the hydration solution pH of the MgO regenerated at 550 °C increased from 8.87 to 10.21 with increased hydration time from 0 to 12 min. The hydration solution pH of MgO regenerated at 1000 °C reached only 7.95 in 12 min and was much lower than that of MgO regenerated at 550 °C. These results indicated that MgO regenerated at low temperatures underwent a much quicker hydration and had a higher reactivity. In contrast, MgO regenerated at high temperatures lost reactivity. This loss was probably caused by the sintering of MgSO<sub>3</sub> particles and the blocking of their pores. The citric acid method evaluated MgO reactivity by the colour transition time of the solution. A quicker colour change corresponded to a higher MgO reactivity. The citric acid method showed the same results as the simplified hydration method in the evaluation of MgO reactivity. Fig. 7 shows that the colour transition time decreased from 263 to 76 s with increased pyrolysis temperature from 450 to 550 °C. The colour transition time then significantly increased with increased pyrolysis temperature. The MgO sample regenerated at 1000 °C had a colour transition time of 532 s, which meant very low reactivity. MgO regenerated at 550 °C had the best reactivity compared with all those regenerated at other temperature ranges. Hence, at low temperatures, MgSO<sub>3</sub> was not completely pyrolyzed. At high temperatures, MgSO<sub>3</sub> was less active because of the sintering of the MgO particles and the blocking of their active sites.

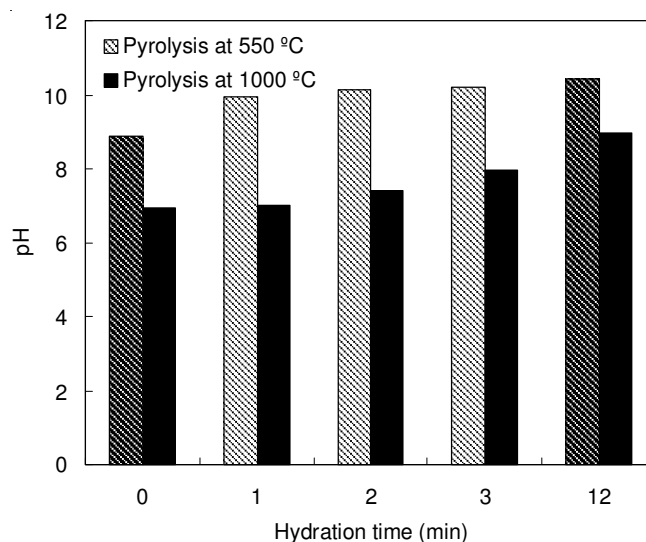


Fig. 6. Changes in the pH of the MgO hydration solution at different pyrolysis temperatures.

Fig. 7. Effect of pyrolysis temperature on the colour transition time of MgO in the citric acid analysis. The XRD analysis gave a comparison of the crystal structure of MgSO<sub>3</sub> pyrolyzed at 550 and 1000 °C. The XRD pattern of MgSO<sub>3</sub> pyrolyzed at 550 °C had a rough baseline with sharp peaks. The peaks under 2θ diffraction angles were irregular, which suggested that the sample pyrolyzed at the lower temperature

had a higher crystallinity. At 1000 °C, the ratio of detection to strongest peaks was 100 and the absorption of full width at half maximum decreased from 0.457° to 0.272°. Apparently, with increased pyrolysis temperature, the crystal size and crystallinity of MgO increased and MgO was easily sintered. Consequently, the reactivity of the regenerated MgO decreased.

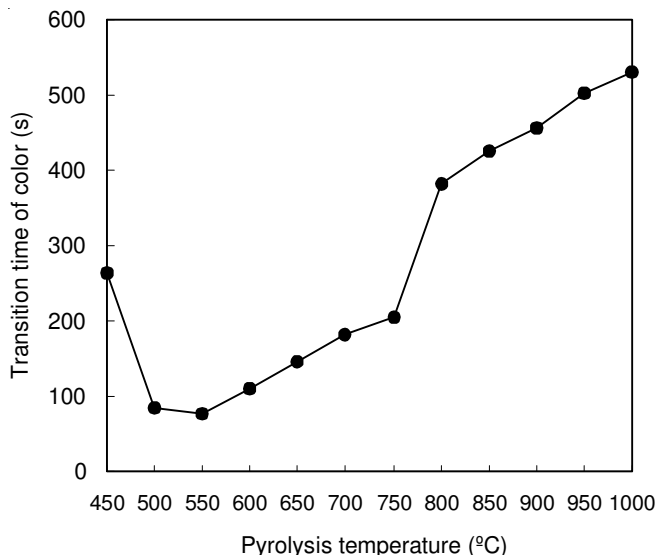


Fig. 7.

**Effect of moisture on MgSO<sub>3</sub> decomposition:** MgSO<sub>3</sub> samples with moisture contents of 0.5 % and 20 % were pyrolyzed at 550 °C for 2 h. Fig. 8 shows that the MgSO<sub>3</sub> samples with 5 % and 20 % moisture produced SO<sub>2</sub> with yields of 74.2 % and 77.0 %, respectively. Both yields were lower than the SO<sub>2</sub> yield from dried MgSO<sub>3</sub> (85.2 %). Fig. 9 shows that with 5 % and 20 % moisture, MgSO<sub>3</sub> decomposition percentage decreased by about 5 % and 10 % compared with dried MgSO<sub>3</sub>. Evidently, moisture was detrimental to MgSO<sub>3</sub> pyrolysis probably because moisture decreased the heat transfer efficiency and diffusion of SO<sub>2</sub> within the MgSO<sub>3</sub> particles.

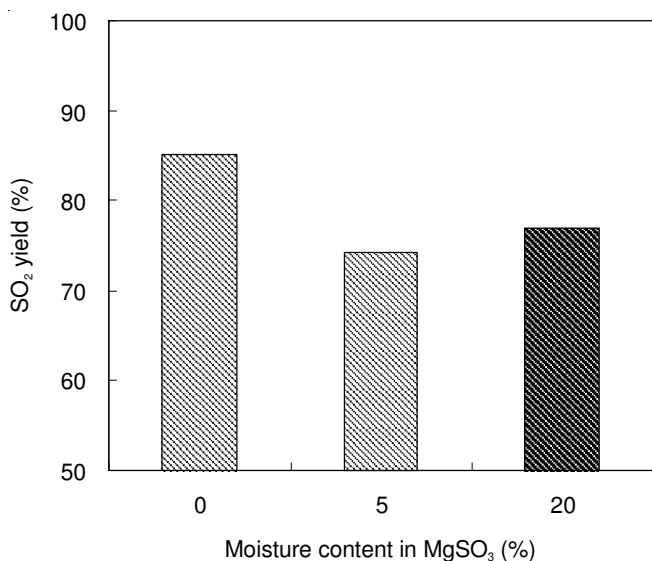


Fig. 8. Effect of moisture on SO<sub>2</sub> yield

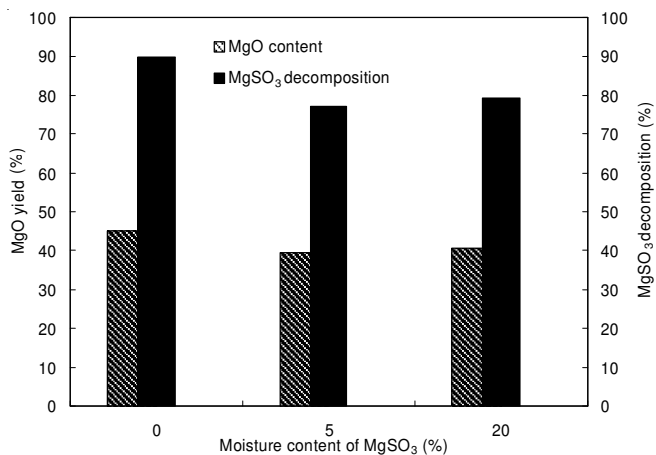


Fig. 9. Effect of moisture on MgO yield

**Effect of moisture on MgO reactivity:** The reactivity of MgO produced *via* MgSO<sub>3</sub> pyrolysis was analyzed by the hydration and citric acid methods. The colour transition time for MgO with 5 % and 20 % moisture were 43 and 40 s, respectively, whereas that for dried MgO was only 23 s (Fig. 10). The hydration method also showed the same results, where the pH of the MgO samples with 5 % and 20 % moisture increased much lower compared with the dried sample (Fig. 11). Apparently, moisture decreased the reactivity of MgO probably because the incomplete decomposition of MgSO<sub>3</sub> produced less gaps between the MgO crystals. In addition, the lattice distortion was not significant because the moisture induced the formation of a compact crystal structure. Hence, drying is essential in increasing the reactivity of recycled MgO.

**Pyrolysis of flue gas desulfurization byproducts from the power plant:** The actual flue gas desulfurization byproducts from the power plant were pyrolyzed at the optimum conditions of 550 °C, 10 K/min heating rate and 23 h pyrolysis time. The flue gas desulfurization byproducts were dried before pyrolysis. The results are given in Table-1.

Based on Table-1, the actual flue gas desulfurization byproducts decomposed under the optimal conditions.

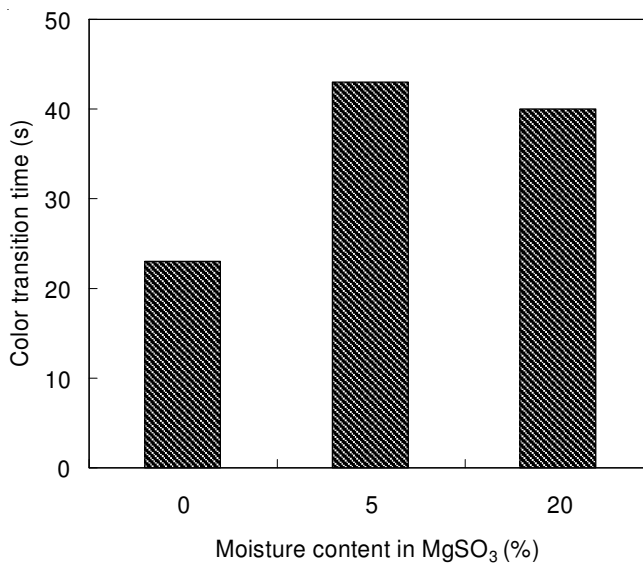


Fig. 10. Colour transition time in the citric acid method analysis of MgO with different moisture contents



TABLE-1  
PYROLYSIS OF THE FGD BYPRODUCTS FROM THE POWER PLANT

	SO <sub>2</sub> yield (%)	MgO yield (%)	Sample decomposition percentage (%)	Colour transition time in citric method (s)
FGD byproduct from the power plant	76.8	31.5	59.5	208
MgSO <sub>3</sub> sample	92.0	43.5	77.1	76

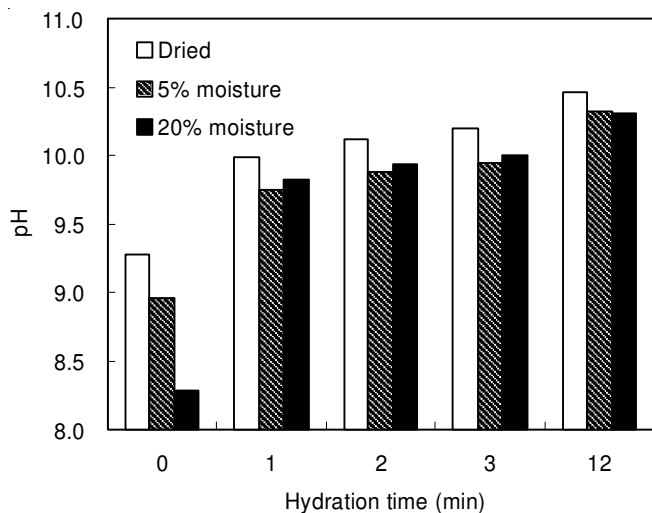


Fig. 11. pH changes during the hydration of MgO with different moisture contents

However, the decomposition percentage was only 59.5 %, which was much lower than that of the laboratory-produced MgSO<sub>3</sub> sample. The actual byproducts had SO<sub>2</sub> and MgO yields that were 15.2 % and 12.0 % lower than those of the laboratory-produced MgSO<sub>3</sub>. The colour transition time in the citric acid analysis for the actual byproducts increased by 132 s, indicating that the pyrolyzed product had a lower reactivity. The flue gas desulfurization byproducts from the power plant probably contained impurities such as dust, which cannot be pyrolyzed. Therefore, in an actual flue gas desulfurization process, dust must be removed to increase the purity of the flue gas desulfurization byproduct to improve the recycling efficiency of MgO.

### Conclusion

MgSO<sub>3</sub> decomposition was significantly influenced by the pyrolysis temperature. At 550 °C and 10 K/min heating rate, the MgSO<sub>3</sub> decomposition percentage and MgO yield reached 90 % and 70 %, respectively. The reactivity of recycled MgO was negatively correlated to the MgO crystallinity. A denser crystal structure corresponded to a less reactive recycled MgO. Moisture was detrimental to MgSO<sub>3</sub> decomposition and

recycled MgO reactivity. Dried MgSO<sub>3</sub> had a higher decomposition percentage and produced more reactive MgO than the samples with moisture. The actual flue gas desulfurization byproducts from the power plant decomposed under the determined optimal pyrolysis conditions. However, the impurities in the byproducts had adverse effects during pyrolysis, ultimately decreasing the yield of SO<sub>2</sub> and MgO. Therefore, impurities such as dust must be removed to obtain a higher amount of highly reactive regenerated MgO.

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